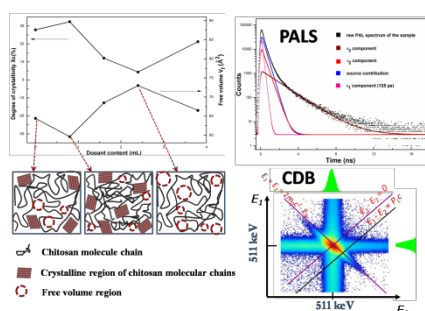


# Probing sub-nano level molecular packing and correlated positron annihilation characteristics in ionic cross-linked Chitosan membrane using Positron Annihilation Spectroscopy

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## Abstract



Chitosan, CS, cross-linked with bivalent palladium has shown enhanced mechanical and thermal properties depending on the transformation of the structure at a microscopic scale. In the present study, CS directly cross-linked by palladium cation membranes (CS-cr-PM) were prepared through solution-casting method. The motion of chitosan chains was great suppressed after crosslinking, making a great reduce of swelling ratio by a water-swelling degree measurement, which led to molecular chain rigidity to be improvement. In order to investigate the chain packing at the molecular level in the ionic cross-linked CS system, the structure of chemically-crosslinked CS is investigated by means of the combined use of wide angle X-ray diffraction (WAXD), Infrared measurements, and a combination of positron annihilation lifetime spectroscopy (PALS) and simultaneous coincidence Doppler broadening (CDB) spectroscopy offers coherent information on both the free-volume related sub-nano level molecular packing and the chemical surrounding of free volume nanoholes in CS-cr-PM as a function of palladium salt loading. The variations in free volume size and size distribution have been determined through the *ortho*-positronium (*o*-Ps) lifetime and its lifetime distribution. The studies showed that strong interaction between CS molecules and palladium cations results in the change of crystallinity in formed CS-cr-PM leading to variational chain packing density. Meanwhile, significant inhibition effects on positronium formation due to doping are observed, which could be interpreted in terms of the existence of chlorid ion. Applications of positron annihilation spectroscopy to study the microstructure and correlated positron annihilation characteristics in ionic cross-linked CS system are systematic discussed.

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## 1.Introduction

Chitosan (CS), a biopolymer constituted by  $\beta$ -(1-4)-linked-2-deoxy-2-amino-D-glucopyranose units, has attracted more and more attentions due to its good biocompatibility, natural availability and the multiple functional groups.<sup>1,2</sup> Moreover, one of the most attractive features of CS that has captured the attention of researchers is the capability to form semirigid films with excellent physical, chemical and mechanical properties. These characteristic, together with its good film-forming capacity, has allowed CS widely used for various functional films material, typical are biosensor membranes, proton exchange membranes, pervaporation membranes and catalytic contactor membranes.<sup>3-8,30</sup> Systematic studies reported shows that, the free volume related microstructural modifications of functional polymeric material altered the molecular packing and are expected to control the bulk properties of the membrane material.<sup>7-14</sup> Therefore, the microstructural modifications in films material are increasingly investigated for the cognition of the evolved microstructure along with the evolved properties. Over the past decades, the study on the relationship between the free volume related microstructure and macroscopic performance (for example, thermal, mechanical, electrical, pervaporation, gas separation and barrier properties) have been one of the main research stream for the polymer film material field, and such studies represent a fundamental step for the understanding of macroscopic properties and can be important for designing new materials with improved properties. Notwithstanding numerous theoretical and experimental investigations focused on the characterization of CS and its complex, structural studies on molecular-level or nanoscale are still scarce, due to the lack of suitable probes for molecular dimensions. In our previous work, CS directly cross-linked by transition metal Pd cation membranes have shown improved mechanical strength and thermal stability, and are considered to be a potential catalyst precursor material for which the Heck cross-coupling catalytic reactions occur inside the unoccupied spaces between macromolecular chains. More importantly, the experimental results show that a correlation dimension matching between the size of free volume nanoholes and molecular of a few typical reactants is closely associated with the catalytic activities.<sup>30</sup> It provides a connection combined the molecular packing of chitosan molecule chains at a microscopic scale using positron annihilation lifetime spectroscopy (PALS) with macroscopic catalytic process. In this regard, an in-depth and careful investigation on the characterization of the polymer (CS)-filler (transition metal palladium salt) complex structure at a microscopic scale becomes essential.

Up to now, increasing number of studies have been conducted probing microstructure in polymeric systems by positron annihilation spectroscopy (PAS) method, for which provides unique molecular-level information about complex macromolecular structure.<sup>15</sup> One of the most common PAS techniques is PALS, which has been developed in the past several decades and proven to be capable of providing information about the free volume and hole properties in polymeric systems, such as size and distribution, directly at the sub-nano level and nanoscale.<sup>18,19</sup> In polymers, followed by implantation of positrons from a radioactive source, a complicated positron annihilation schemes involving positronium (Ps) formation can occur, Ps is a hydrogen-like state and corresponding to mutual spin orientations (parallel and anti-parallel) of the consisting particles including exist in the form of singlet spin state *para*-positronium (*p*-Ps) and triplet spin state *ortho*-positronium (*o*-Ps). The intrinsic lifetime of *p*-Ps is only 125 ps, whereas in vacuum, the intrinsic lifetime of *o*-Ps is 142 ns. In molecular solids like polymers, *o*-Ps has a relatively small diameter (0.106 nm), the trapped *o*-Ps is localized in free volume nanohole, and the observed lifetime of *o*-Ps annihilates in some nanoseconds on an electron from the surrounding media (the so-called pick-off process). Hence by using PALS, *o*-Ps has been widely applied as a chemical probe for molecular environment and in particular to the free volume nanoholes in which it is localized, a distribution over the *o*-Ps lifetime is usually measured to determine the free volume nanoholes size distribution and the high sensitivity of *o*-Ps to low-density regions (inter- and intra-chain space of the polymer) is well documented.<sup>16-29</sup> It is based on the fact that the PALS are widely used to understand the correlation between the molecular-level structural changes in

the polymer matrix in terms of the *o*-Ps as structural probe (positron annihilation parameters as structural parameters) and the macroscopic performance. On the other hand, a precise analysis and characterization of the microstructure of polymer is thus strongly required for the understand of the related positron annihilation mechanism. A better understanding of the positron annihilation characteristics or the more meaningful interpretation of positron annihilation parameters in specific material is very important for the molecular insight and leads to a broad application of the PAS.

In spite of lots of researches on application of PALS on functional polymeric material have been proceeding, however, lifetime spectroscopy cannot provide information on the chemical surrounding at the annihilation site, and thus the positron annihilation characteristics and free volume related microstructure have often been studied separately. Positron annihilation in polymer carry significant information about the molecular structure, for a better understanding of the mechanism of the rather complex physical scenario occurring in the positron annihilation process in polymer, it is necessary to apply a more sensitive physical method which can supply complementary information. It has been shown that the positron coincidence Doppler broadening (CDB) is such a unique technique.<sup>20,37,40</sup> For years a conventional broadening Doppler spectrum has been widely used to give important information about the momentum distribution of the annihilating electrons.<sup>41</sup> A thermalized positron in the material annihilates with an electron, emitting two  $\gamma$  photons of 511 keV in opposite direction. These two  $\gamma$  photons are Doppler broadened by  $\Delta E = P_L c$  ( $P_L$  and  $c$  being the annihilating electron momentum in the detector direction and the velocity of light, respectively) in the theoretical frame, depending on the energy of the annihilating electron. It is well-known that the low momentum part of the spectrum arises mainly from the annihilation with the valence electrons and the core electrons contribute to the high momentum part of the spectrum. However, one visible drawback is that a very small fraction of positrons annihilate with core electrons due to the strong repulsion of positron by the positively charged nucleus, and hence the high momentum component is often buried in the background of the spectrum. A relatively new development Coincidence Doppler broadened technique can settle this problem well, since it is capable of eliminating the background to a great extent. This enables unambiguous magnification of the shape and magnitude of the high momentum core component.<sup>39-41,47</sup> Therefore, a combined use of CDB measurement is principally very valuable since it involves quantitative information on the detailed electron momentum distribution at positron annihilation site and thus can be further utilized to determining the chemical environment of the annihilation site.<sup>35-41,47</sup> Recently, some works were focused on the characterization of evolved sub-nano and nano level molecule packing in polymer nanocomposites system, typical are, effect of interfacial interaction on the free volumes in polymer nanocomposites.<sup>31-34</sup> In these studies, CDB measurements are carried out, and confirmed that can be used to extract information about the polar groups and chemical surroundings of the free volume nanoholes in polymer nanocomposites system.<sup>20,29</sup> Therefore, It turns possible to directly obtained more information about microstructure property through a combination of PALS and CDB technique.

In the present study, we have chosen a divalent metal palladium salt and dope with different content to the polymer CS. The effect of palladium salt doping on the microstructural properties were studied using WAXD, FTIR and PALS as well as CDB techniques. PALS was employed to characterize the sub-nano level free volume size and size distribution as a function of palladium salt loading. The comparison analysis of CDB spectra on PC, PEI and CS illustrate the methodology of CDB data analysis in polymer. A combination of PALS and simultaneous CDB spectroscopy offers coherent information on both the free volume related molecular packing and the chemical surrounding of free volume nanoholes. The sub-nano level molecular packing and correlated positron annihilation characteristics in cross-linked CS network were systematically investigated.

## 2. Experimental Section

## 2.1 Specimen Preparation

The polymer film samples purchased from Goodfellow (Cambridge, UK), including Polycarbonate (PC), Polyetherimide (PEI). Chitosan was supplied by Zhejiang Shaoxing Biotechnology with its deacetylated degree was about 99%, and the average molecular weight ( $M_w$ ) was  $1.2 \times 10^5$ . All of the chemical reagents used in our study were of analytical grade. For preparing ionic cross-linked CS membrane, chitosan (0.8 g) was dissolved in 40 mL of 2 wt% acetic acid solution at room temperature under magnetic stirring for about 6h and then ultrasonic treatment for about 30 min. Simultaneously, certain concentration  $\text{Na}_2\text{PdCl}_4$  solution was prepared by dissolution of 0.15 g of  $\text{PdCl}_2$  and 0.75 g of NaCl together in 50 mL of deionized water. Selected certain volume of salt solution were slowly dropped into the chitosan solution under magnetic stirring, the obtained solution was then cast on glass Petri dish and remove the air bubbles trapped in the viscous liquid. The mixed solution was then dried at 300 K in drying oven, the formed films were soaked with distilled water and ethanol to remove the residual solvent. Finally, the as-prepared membranes were again dried under vacuum for 10 h. The membranes contained 0, 0.8, 1.6, 2.4 and 3.2 mL volume of salt solution are referred to as CS and CSPD1-4, respectively. In addition, for the contrast experiment, chitosan powder (1g) was modified with palladium by adsorption of above different volume (0, 2, 5, 7 mL) of salt solution from neutral solutions on the surface of chitosan molecule, and they are referred to as CS-0, CS-2, CS-5 and CS-7, respectively.

## 2.2 Characterization

The crystalline structure of as-prepared membranes were investigated with an X-ray diffractometer (Rigaku XRD-3 Pgeneral, Cu K $\alpha$ , 40kv, 40mA) in the range from 10 to 45°. From the scanned XRD graphs, the degree of crystallinity  $X_c$  (%) was estimated from the Eq.(1).

$$X_c = \frac{A_{\text{cry}}}{A_{\text{cry}} + A_{\text{amor}}} \times 100 \% \quad (1)$$

where  $A_{\text{cry}}$  and  $A_{\text{amor}}$  are the area of crystalline and amorphous region, respectively. The Fourier Transform infrared spectroscopy (FTIR) of the samples were measured by using a Thermo Scientific Nicolet IN10MX instrument with a liquid-nitrogen cooled detector from wave number range of 750-4000  $\text{cm}^{-1}$ . The swelling properties of the sample in water were determined according to the following procedure. The membrane samples were immersed in water (40 °C), and then taken from the solution at different interval times. After removal of the surface excess water, the ratio of water absorption ( $S_a$ ) at an instant time  $t$  can be calculated according to Eq.(2).

$$S_a = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the membrane sample weights at the interval time  $t$  and 0, respectively.

## 2.3 Positron Annihilation experiments

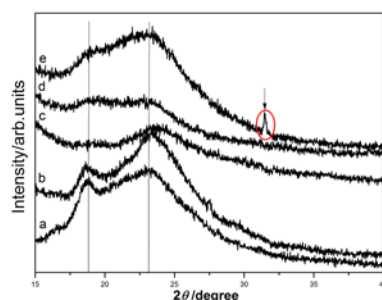
The as-prepared samples were heated at 35 °C for 10 h before carrying out the measurements to remove the absorbed water from the samples. The positron annihilation lifetime measurements were carried out at room temperature using a standard fast-slow coincidence system with a time resolution of about 210 ps (FWHM). The positron source ( $^{22}\text{Na}$ , 16  $\mu\text{Ci}$ ) was carrier free NaCl deposited between two 7  $\mu\text{m}$  thick Kapton foil, and then sandwiched in two stacks of identical pieces of samples (with a diameter of 1 cm and a thickness of 1.5 mm) ensuring that all positron annihilate within the sample. All the positron lifetime spectra were recorded with total counts contained  $\sim 3.5 \times 10^6$ . A single crystal silicon was used to calculate the fraction of positrons annihilating within the source and kapton foils. Source components were obtained and were corrected in the analysis of positron lifetime spectra of the samples. The routine LT-9 was used for analysis of the positron lifetime spectra and taking into account the annihilation in the source, all of the collected polymer spectra were analyzed by three

exponential components. The analysis was carried out by fixing the  $p$ -Ps component (125 ps) and the variance of the fit is around 1.0. The routine MELT was used to evaluate the distribution function of annihilation rate from the lifetime spectrum.

A higher activity positron source ( $^{22}\text{Na}$ , 28  $\mu\text{Ci}$ ) sandwiched between two kapton foils of thickness 7  $\mu\text{m}$  was used for the CDB measurement at room temperature. Two identical HPGe detectors located at  $180^\circ$  relative to each other were used to detect the coincident annihilation  $\gamma$ -rays emitting from a single event (denoted by  $E_1$  and  $E_2$ ). The difference in the energies of annihilating  $\gamma$ -rays pairs,  $E_1 - E_2$  is expressed as  $cP_L$ , and the total energy  $E_1 + E_2$  is expressed as  $2m_0c^2 - E_B$ , where  $P_L$  is the longitudinal component of the positron-electron momentum along the direction of the detector,  $m_0$  is the electron rest mass,  $c$  is the speed of light and  $E_B$  means approximately the electron binding energy. To obtain the annihilating electron momentum distribution, CDB spectra were recorded with the total counts being about  $1.2 \times 10^7$  in the coincidence  $512 \times 512$ -channel matrix. Selection of coincidence events that fulfilled the condition  $2m_0c^2 - 2.2 \text{ keV} < E_1 + E_2 < 2m_0c^2 + 2.2 \text{ keV}$  (the Doppler shift 1 keV corresponds to  $P_L = 1.956 \times 10^{-3} m_0c$ ), which resulted in a significant improvement in the peak to background ratio. Each CDB spectrum was normalized to unit area and divided by a reference sample to get the ratio curve.

### 3. Results and Discussion

The polymer–transition metal salt composites are characterized by interaction of the transition metal with the polar group of the polymer, which gives rise to complex formation.<sup>21</sup> The microstructural variations of CS upon the incorporation of palladium salt are investigated using WAXD. Fig. 1 shows the XRD pattern of pure CS and its variation with palladium salt incorporation. CS is a kind of semi-crystalline polymer, in agreement with the most report, the pure CS exhibits two typical characteristic peaks, the peaks at  $2\theta$  of  $18^\circ$  and  $23^\circ$ , which are assigned to anhydrous crystalline and amorphous structure of CS.<sup>20</sup> On the initial stage of doping (CSPD1), interaction between polar groups of chitosan molecule ( $-\text{NH}_2$ ,  $-\text{OH}$ ) and Pd cations may contribute to a relatively ordered

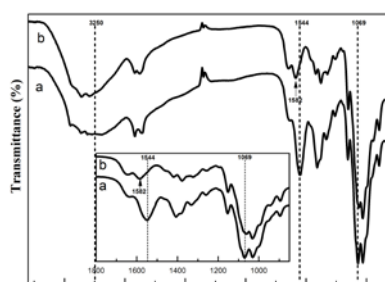


**Fig. 1** XRD spectra of pure CS (a), and CS based complex having different palladium salt content, CSPD1 (b), CSPD2 (c), CSPD3 (d), and CSPD4 (e).

arrangement of molecule chains. A slight enhancement in the intensity of the CS characteristic peaks were thus observed. On increasing the content of palladium salt, a sharp decrease in the intensity of the characteristic peaks from CSPD1 to CSPD3 was observed, indicating the change in crystallinity or molecular packing of CS. The results showed that with the increment of palladium salt content, the relative crystallinity of the obtained CS would first increase and then decrease. In these observations, no new peaks appeared, verifying that Pd existed in CS network in an amorphous form. On higher loading of palladium salt content (CSPD4), an inconsistency law of experiment result was observed, such a result is reasonable due to chitosan solution reaches the gelation point, which influence the homogeneously dispersed of dopants. An obvious new diffraction peak (marked by downward

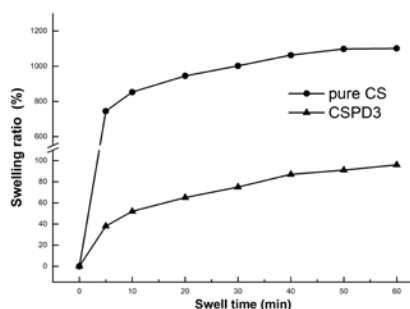
arrow) are also observed, thus giving a clear indication of formation of dopant aggregates, and this peak can be indexed to characteristic peak of NaCl. Upon incorporation of palladium salt, there were almost no crystalline peaks observed in the XRD patterns of CSPD3, indicating the great change of molecular structure of chitosan in this case.

To investigate more about the chemical changes in the doped chitosan matrix. A spectral characterization of the CS and CSPD3 is provided in Fig. 2. The FTIR spectrum of CS exhibits the following characteristic peaks: peaks appear at 3200-3500  $\text{cm}^{-1}$ , ascribed to the typical of overlapping of N-H and O-H stretching of CS. The



**Fig. 2** FTIR spectra of (a) CS and (b) CSPD3. The inset shows the fingerprint region from wave number range of 1600-850  $\text{cm}^{-1}$ .

absorption band at 1544  $\text{cm}^{-1}$  and 1636  $\text{cm}^{-1}$ , attributed to the stretching vibration N-H and bending vibration of C=O, respectively. The absorption band at 1069 and 1022  $\text{cm}^{-1}$  corresponded to the stretching vibration of OH-C<sub>3</sub> and OH-C<sub>6</sub> groups of CS. Comparison of the FTIR spectrum of CSPD3 with that of CS shows Pd cations bonding causes a noticeable sharper in the shape of the absorption line at 3200-3600  $\text{cm}^{-1}$ , this indicates a weakening of the intermolecular hydrogen in cross-linked CS. Moreover, there is substantial redistribution of vibration frequencies in fingerprint region when Pd cations were introduced into chitosan matrix. The inset shows the N-H bending vibration band shift from 1544  $\text{cm}^{-1}$  to higher wavenumbers 1583  $\text{cm}^{-1}$ , and the intensity of these band in cross-linked CS decreases to a certain extent, such upward overall shift means the presence of a steric effect from bending vibration of the N-H bond after coordinating. In addition, the stretching vibration frequency of C-O shifts from 1069 to 1056  $\text{cm}^{-1}$ , this downward shift accompanying a decrease in intensity indicate the reaction of Pd cations with OH-C<sub>3</sub> functional groups of CS. These observations suggest that the O (OH-C<sub>3</sub>) and N atoms (—NH<sub>2</sub>) in chitosan of the palladium(II)-chitosan coordination polymer participated in coordination with palladium, which is in good agreement with former studies investigating similar systems.<sup>42,46</sup>



**Fig.3** Swelling ratios of the CS and CSPD3 in water solutions.

In our previous work,<sup>30</sup> macroscopic performance reports are available on ionic cross-linked CS where the mechanical and thermal properties are shown to be enhanced on palladium salt incorporation. It is generally known that doping is an effective way of tailoring the polymeric properties for a particular application. When a polymer is doped, the dopant can induce modifications in the molecular structure depending on the way in which they interact

with the host polymer.<sup>21</sup> The interaction between the polar group of the CS and the transition metal Pd cations, in particular, have the ability to induce modifications in the chitosan molecular structure and leads to an altered microstructural property. Therefore, the reason behind the enhancement of these physical properties are supposed to be closely related with the rearrangement of molecular chains. In order to study the effect of palladium salt incorporation on the bulk property of the as-obtained ionic cross-linked CS membrane, swelling degree measurement were carried out. Fig. 3 compares the water-swelling properties of the prepared CS and CSPD3. Examination of Fig.3 shows the water absorption could reach equilibrium within 60 min. It is clear that pure CS is easier to swell, and the swelling ratios of the pure CS far greater than cross-linked membrane under the same water adsorption time. The maximum swelling ratios of the prepared CS and cross-linked CS membranes were determined to be about 11 and 0.9, respectively. Meanwhile, the area of the pure CS membrane becomes bigger than cross-linked CS after the water absorption, thus the experimental results reveal that the cross-linked network can limit the movement of the molecular chains to make the molecular chain rigidity to be improvement. On the other hand, the Pd cations bound to several hydrophilic polar groups in a chitosan chain (intrachain effect) or bounding with other chains act as cross-links (interchain effect) makes the reduction of the number of hydrophilic groups. Therefore, the great reduce of swelling ratio is supposed to be attributed to the synergistic effect of these two factors as mentioned above.

Table 1. Results from LT-9 analysis.

Quantity	$\tau_1$ (ps)	$I_1$ (%)	$\tau_2$ (ps)	$I_2$ (%)	$\tau_3$ (ns)	$I_3$ (%)	$R$ (Å)	$V_f$ (Å <sup>3</sup> )
Statistical error	$\pm 0.0$	$\pm 0.3$	$\pm 0.15$	$\pm 0.3$	$\pm 0.01$	$\pm 0.1$	$\pm 0.001$	$\pm 0.1$
CS	125	29.27	371.4	55.76	1.6279	14.97	2.487	64.4
CSPD1	125	28.74	347.7	60.52	1.5701	10.74	2.423	59.6
CSPD2	125	30.21	347.1	61.34	1.6766	8.45	2.539	68.5
CSPD3	125	31.62	341.2	60.22	1.7290	8.26	2.593	73.0
CSPD4	125	28.41	341.2	64.67	1.6530	6.93	2.513	66.5

Palladium catalyst entrapped within the CS membrane have shown highly efficient and stable properties for Heck Reactions depending on their interaction with CS molecules and the size and size distribution of free volume nanoholes in cross-linked CS gel network.<sup>30</sup> To study the effect of the strong interaction on microstructural transition in cross-linked CS system, PALS technique as a unique direct way to probe the free volume related microstructure was employed. The program LT-9 is used to fit the PALS spectra to evaluate the distribution of lifetimes. The lifetime and intensity of the three components,  $\tau_1$  ( $I_1$ ),  $\tau_2$  ( $I_2$ ), and  $\tau_3$  ( $I_3$ ), correspond to those of shortest lifetime component (*p*-Ps), the intermediate lifetime component (without the formation of Ps), and the longer pick-off annihilation of the *ortho*-positronium (*o*-Ps) component, respectively. It is well-established view that the *o*-Ps lifetime is sensitive to the molecular environment and in particular to the mean whole size of the free volume spaces where it is localized, and thus the densification of molecular arrangement reduces the free-volume region available for *o*-Ps and leads to a decrease in mean lifetime  $\tau_3$ .<sup>20,29</sup> In the case of cross-linked CS gel network, a semicrystalline CS consisting of crystalline and amorphous phases in the bulk polymer matrix, which may be regarded as an amorphous matrix in which a certain orderly crystal-like arrangement are randomly distributed, and the *o*-Ps lifetime provides important information about the nanocavity and free volume related microstructures in membranes. The discrete positron lifetime components for all of the samples can be well decomposed into three components and the corresponding results are shown in Table 1. The obtained *o*-Ps annihilation lifetime can be transformed to radius and volumes of free volume cavities or holes through Equation (3) and (4) based on the

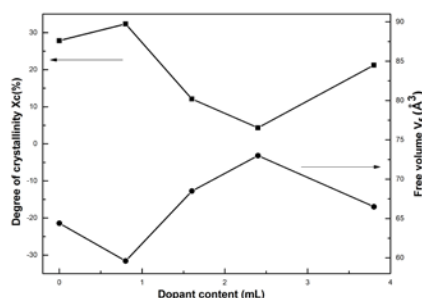


Tao-Eldrup free volume model.<sup>27,28</sup>

$$\tau_3^{-1} = 2 \left\{ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R + \Delta R} \right) \right\} \quad (3)$$

$$V_f = \frac{4\pi R^3}{3} \quad (4)$$

in which  $R$  is the average radius of the free volume cavity,  $\Delta R = 1.656 \text{ \AA}$  is derived from fitting the observed *o*-Ps lifetimes in molecular solids (an empirical parameter),  $V_f (\text{\AA}^3)$  is the average size of the free volume cavities.



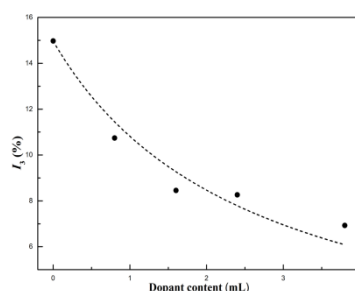
**Fig.4** Variation of crystallinity and average free volume nanoholes size as a function of palladium salt content in CS.

The *o*-Ps lifetime obtained from a finite  $\times 3$ -fitting procedure observed for pure CS is in good agreement with the report by Chaudhary and K.Sharma.<sup>17,20</sup> When a small amount of palladium salt were added into the CS matrix (CSPD1), the packing modes of molecular segments were partly rearranged, and a large amount of segmental chains become relatively ordered arrangement (contribution to crystallinity as observed in WAXD), leading to the densification of molecular arrangement. As expected we observe an evident decrease in value of  $\tau_3$  as shown in Fig. 4. A similar type of change has been observed in the local orderly arrangement of chitosan on incorporation of little amount of NiO as filler.<sup>20</sup> In addition, it is interesting that the obtained value of  $\tau_3$  are found to be correlated well with the degree of crystallinity ( $X_c$ ) of formed ionic cross-linked CS membrane. Consequently, the result of average size of the free volume cavities, calculated in terms of the mean lifetime  $\tau_3$  of *o*-Ps and reflects the compactness of molecular arrangement fluctuations within a polymer, as a function of palladium salt content are plotted in Fig. 4. The inverse relationship between the average nanohole size  $V (\text{\AA}^3)$  and the degree of crystallinity ( $X_c$ ) indicates that the whole compactness of chitosan molecular arrangement can be directly related to the crystallinity of formed CS complex film. Hence, it is revealed that a direct relationship among of the *o*-Ps lifetime, relative crystallinity and the densification of chitosan molecule chains could be established in this case. These results indicate the size of free volume nanoholes in cross-linked CS gel network increases or decreases basically according to the proportion of crystalline phase (or are highly ordered molecular arrangement regions) in the bulk chitosan matrix, and the densification (or sparsification) of molecular packing reduces (increasing) the free-volume region available for *o*-Ps and leads to a decrease (or an increase) of mean lifetime  $\tau_3$ . That is to say, the regulation of free volume property of CS complex film can be well realized by changing its relative crystallinity, and this can be done by controlling the amount of added palladium salt.

From various studies it is clear that *o*-Ps atoms tend to localize in the amorphous regions and crystalline-amorphous interfaces (that is the so-called free volume holes according to the free volume model) of a semicrystalline polymer.<sup>40</sup> It is a well-established view that the formed *o*-Ps can be widely used as a chemical probe for directly determining the sub-nano or nanometer scale free volume holes (by the parameter of *o*-Ps lifetime), and their number density or concentration fluctuations (by the corresponding parameter of *o*-Ps intensity)



within a polymer. Therefore, a correlation between the molecular ordering by density fluctuations due to crystallinity of the samples and the *o*-Ps formation probability  $I_3$  is often expected.<sup>18,19</sup> However, in the present case a continuous decrease of  $I_3$  intensity from 14.97 % in CS to 6.927 % in CSPD4 was observed in Table 1. The result shows that the behavior of the  $I_3$  variations with the dopant content is not only simply associated with the factor of microstructure, but also to further considering the correlated positron annihilation characteristics. Generally, the decrease in *o*-Ps intensity can be observed as a result of two types of possible characteristics in polymer: (1) a decrease in the number of places suitable for *o*-Ps atoms annihilation (relative free volume concentration), (2) a decrease in the probability of Ps formation (*o*-Ps inhibition). A monotonic decrease of  $I_3$  intensity indicates that it is difficult to pinpoint the first excuse for the decrease of  $I_3$  intensity. Hence, the decrease supports the possibility of positronium formation inhibition in the cross-linked CS system.



**Fig. 5** The *o*-Ps intensity ( $I_3$ ) as a function of palladium salt content in CS. The dotted line is the fit variation of  $I_3$ .

Many researchers reported that both cations and anions could provide a competing characteristics of Ps formation in terms of the spur reaction model.<sup>35-38</sup> In the doped CS system, the Ps inhibitor for cations ( $\text{Pd}^{2+}$ ) and anions ( $\text{Cl}^-$ ) are available, it is possible that trapping either of  $e^+$  ( $\text{Cl}^-$ ) or  $e^-$  ( $\text{Pd}^{2+}$ ) are supposed to make the positron having less chance to form Ps atom in the local environment. The Ps inhibition characteristics which can significantly reduce  $I_3$  has been reported in the literature and the variation of  $I_3$  is often given by the following equation:<sup>38</sup>

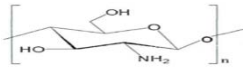
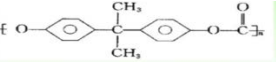
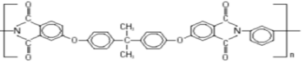
$$I_3 = I_0 / 1 + (\alpha C)^\beta \quad (5)$$

where C represent the content of inhibitor,  $\alpha$  and  $\beta$  called inhibition constant, and  $I_0$  the ideal *o*-Ps yield assuming  $\alpha=0$ . In our case, Fig. 5 shows the variation of  $I_3$  intensity as a function of palladium salt content, the variation of  $I_3$  with the content of palladium salt can be well fitted to  $Y = b / 1 + aX$ , where  $I_0$ ,  $\alpha$  and  $\beta$  are evaluated corresponding to be 14.97 (b), 0.38 (a) and 1, respectively. The result further confirms the possibility of *o*-Ps inhibition in the doped CS system. Taking into account for the chemical sensitivity of the coincidence Doppler broadening of annihilation radiation, we try to extract coherent information on both the chemical neighborhood of the positron annihilation sites and the chemical surrounding of nanoholes in ionic cross-linked CS system by CDB measurements. For this purpose, so we first need to analyze the related positron annihilation characteristics in complex CS polymer system.

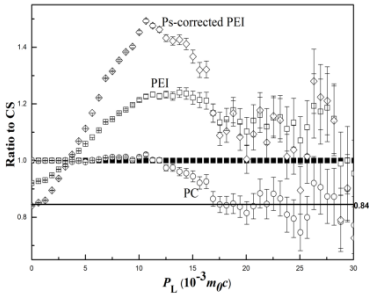
Theoretically speaking, the CDB technique is capable of identifying the chemical surrounding of the annihilation site and being element sensitive, and can be used to provide information about the polar groups and chemical surrounding of nanoholes in polymer.<sup>20,29,30</sup> Previous many studies showed that the ratio curve of the CDB spectrum for experimental sample to that of reference sample reflects the difference of momentum density distribution of the electrons taking part in the annihilation processes in different environment. It is commonly accepted that CDB spectra are presented as a ratio to the chosen reference spectrum, and the chemical surrounding of the annihilation site or elemental specificity can be extracted from the shape and magnitude of the CDB spectra.<sup>39-41,47</sup> To obtain more information about the positron annihilation in CS and illustrate the methodology of CDB

data analysis in polymer system, CDB measurements have been carried out in CS, oxygen-containing Polycarbonate (PC), nitrogen-containing Polyetherimide (PEI) and the corresponding PALS result is shown in Table 2.

Table 2. The extracted parameters obtained from LT-9 analysis and corresponding calculated free positron annihilation fraction  $f$  and chemical structure for CS, PC and PEI.

Sample	$\tau_1$ (ps)	$I_1$ (%)	$\tau_2$ (ps)	$I_2$ (%)	$\tau_3$ (ns)	$I_3$ (%)	$f=1-4/3 I_3$	Chemical structure
CS	125	29.27	371.4	55.76	1.6279	14.97	0.801	
PC	125	33.91	398.2	41.44	1.7350	24.65	0.671	
PEI	125	33.38	384.5	63.52	1.6940	3.21	0.958	

The parameter  $f$  is the fraction of positron not forming Ps in polymer, and shows positron annihilation based on the free positron annihilation mode. It is a well-established view that the high-momentum component of CDB spectra is associated with the annihilation of free positrons in polymer owing to the formed Ps could not be able to penetrate deeply in the constituent atoms due to the molecular repulsion force.<sup>33,40,47</sup> Therefore, the formed o-Ps are not able to change the high-momentum CDB component, and hence studies focused on the fraction of positron annihilation based on free positron annihilation mode in polymer is of profound importance. The measured CDB ratio curves of PC and PEI to pure CS are presented in Fig. 6. These ratio curves show notably variation in high



**Fig. 6** CDB ratio curves of PC (○), PEI (□), and Ps-corrected CDB ratio of PEI (◇) with respect to CS.

momentum region, for which core electrons contribute mainly from free positron annihilation. The ratio curve for PC coincide exactly with the CS in momentum region before reaching  $\sim 11 \times 10^{-3} m_e c$ , while showing almost parallel to X-axis in higher momentum region, and the Y-axis differentials (0.84) exactly equal the ratio of fraction of positron annihilation (as calculated from Table 2,  $f(\text{PC}/\text{CS}) = 0.839$ ) for CS and PC. It is known that the CDB ratio curve would have been a straight line parallel to X-axis in the high momentum part and the ratio of them equals to the corresponding ratio value of the fraction of positrons if there were no change of chemical environment for positron annihilation in polymer.<sup>47</sup> Thus, this result demonstrate that the positrons annihilation characteristics could be considered as analogous in CS and PC matrix from the electron momentum point of view, and the differences of the intensity of two ratio curves were determined by the fraction of positron annihilation based on free positron annihilation mode in samples. A problem appears, if we try to compare the CDB ratios of different elements of polymer, PC is consist of carbon, hydrogen, oxygen and while CS in a more element that is

nitrogen, the expected ratio curve should have highlighted more information about N elements, since the core electron momentum distribution is not influenced by the chemical and physical state of the element, and the CDB technique is capable of identifying the element irrespective of the the chemical and physical state of the element present in the sample.<sup>41</sup> It appears as if the chemical environment for positrons annihilation is irrelevant to the N element in CS.

To make further illustration, CDB ratio curve of nitrogen-containing polymer (PEI) was also used for comparison, a broad peak is observed at  $\sim 12.5 \times 10^{-3} \text{ m0c}$ , which shows a great difference with PC. In most case, a Ps correction is necessary due to the different fraction of the free positron annihilation in the sample and reference.<sup>47</sup> In this, a Ps-corrected is necessary because, as can be seen from Table 2, the calculated  $f$  parameter values indicate clearly difference in the Ps contribution from the CS and PEI. In various studies, the momentum density distribution obtained from CDB can be composed into free positron and positronium contributions.<sup>20,29,39-41</sup> Thus the way to analyze properly on the peak shape of CDB is first to exclude the Ps contribution from the sample and reference by Eq.(6).

$$N(P_L) = (1 - f) N_{Ps}(P_L) + f N_{e^+}(P_L) \quad (6)$$

Here,  $P_L$  refers to the momentum component of the positron-electron pair in the direction of the detectors.

In order to get much more precise visual comparison on CDB, we, therefore, attempted to analyze the CDB spectra of PEI considering PC and CS as standard samples due to the annihilation process in CS and PC could be considered as analogous as mentioned above. A similar process has been reported by Yu et al.<sup>39</sup> According to Eq.(6), we can write

$$N^{CS}(P_L) = \frac{4}{3} I_3^{CS} N_{Ps}^{ref}(P_L) + (1 - \frac{4}{3} I_3^{CS}) N_{e^+}^{ref}(P_L) \quad (7)$$

$$N^{PC}(P_L) = \frac{4}{3} I_3^{PC} N_{Ps}^{ref}(P_L) + (1 - \frac{4}{3} I_3^{PC}) N_{e^+}^{ref}(P_L) \quad (8)$$

where  $N_{Ps}^{ref}(P_L)$  and  $N_{e^+}^{ref}(P_L)$  are the reference sample's contribution from Ps and free positron annihilation, respectively. Assuming that there is no distinction in the Ps annihilation curves for the PEI sample and reference sample, we can write

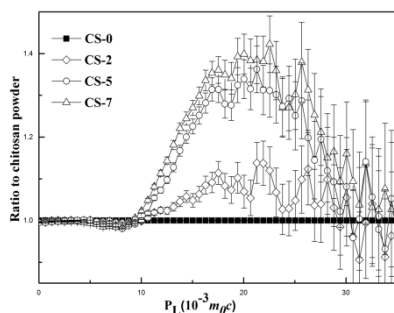
$$N^{PEI}(P_L) = \frac{4}{3} I_3^{PEI} N_{Ps}^{ref}(P_L) + (1 - \frac{4}{3} I_3^{PEI}) N_{e^+}^{ref}(P_L) \quad (9)$$

The normalized ratio curve for PEI was calculated as follows:

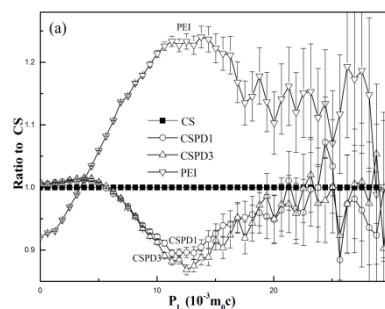
$$\text{Ratio}^{PEI}(P_L) = \frac{N_{e^+}^{PEI}(P_L)}{N_{e^+}^{ref}(P_L)} \quad (10)$$

the obtained Ps-corrected PEI CDB ratio (Fig. 6) shows a evident peak at  $\sim 12 \times 10^{-3} \text{ m0c}$ . Consequently, combining the CDB results of PC and PEI, this ensures that the observed sharp peak can be treated as due to the annihilation of positrons on nitrogen atom. It may be mentioned that similar observation peak of annihilation of positron with N atom in  $\text{Si}_3\text{N}_4$  has been reported by Sachdeva et.al.<sup>41</sup> The above result shows that at CS network, the most probable annihilation site for free positron trapping is deviate from the N atom. This clearly indicates that free positrons are not trapped at the polar groups ( $-\text{NH}_2$ ) and mainly annihilate from relatively enriched C, H and O atoms which are associated with the D-glucopyranose ring moieties of chitosan backbone. It is tempting to describe this to the protonation of amino groups in film-forming process that leads to nitrogen-containing amino group being electropositive carries and localization of positron wave function, and consequently decrease in its overlap with the positively amino groups.

To make a further illustration of the positron annihilation characteristic in ionic cross-linked CS system, CDB measurements have been carried out in CS, CSPD1, CSPD3. The normalized CDB ratio curves are shown in Fig. 8. The ratio curves for CSPD1 and CSPD3 show significant changes from CS indicating different chemical

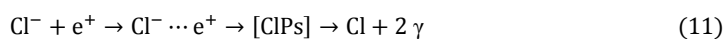


**Fig. 7** CDB ratio curves for CS-2( $\diamond$ ), CS-5( $\circ$ ), and CS-7( $\Delta$ ) relative to pure chitosan powder CS-0( $\blacksquare$ ).



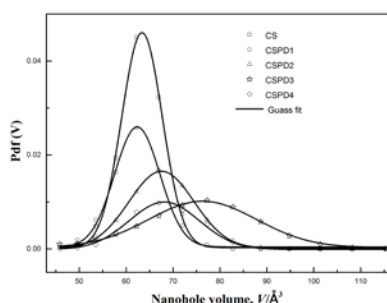
**Fig. 8** Ratio curve of CDB spectra for CSPD1, CSPD3 and PEI relative to CS.

surrounding for positron annihilation. As mentioned above, it is noteworthy that the CDB shape obtained for the polymer system is susceptible to the constituent of element, fraction of the free positron annihilation (Ps contribution) from the sample and reference. Notably, Ps contribution could be excluded in cross-linked CS, since as the  $I_3$  decrease (as can be seen from Table 1), the  $f$  value increase and CDB profile in the high momentum regions should have upturned, contrary to what is presented in Fig. 8. In addition, Fig. 7 shows the ratio curves of CDB spectra for chitosan powder containing adsorbed palladium species (CS-2, CS-5, CS-7) relative to no adsorption (CS-0). As in the case of adsorption experiments, different content of adsorbent palladium solution was directly absorbed by chitosan powder. A systematic increase in the peak with the amount of adsorption of palladium is indicative of the increase in overlap of positron wave function with the palladium semi-core electron. This experimental result shows that CDB spectroscopy is a good element-sensitive tool and the semi-core electrons for added palladium element are supposed to have a large contribution in high momentum region. However, contrary to the above fact the ratio curves for the ionic cross-linked CS system (Fig. 8) are evidently reverse. The figure shows that positrons do not annihilate from the added element in ionic cross-linked CS system. In the case of ionic cross-linked CS system, a evident increase in the area under lower momentum region ( $0 \times 10^{-3}$  to  $6 \times 10^{-3} m_0c$ ) is observed, indicating more positron trapping at surface relatively enriched C and H atoms having low contribution in the higher momentum region. On the other hand, depending on the abundant amino and hydroxyl groups of the chitosan molecule, a cross-linking of the chitosan chains through the transition metal cation chelation with the surrounding amino, carbonyl, and hydroxyl functional groups either in linear or in three-dimensional networks has been reported.<sup>43</sup> Consequently, the decrease in the area under the ratio curves under high momentum region from  $6 \times 10^{-3}$  to  $20 \times 10^{-3} m_0c$ , which is opposite to the peak of PEI, indicates the reduction in contribution from N in  $-NH_2$  groups. The above CDB results indicate that most probable chemical surrounding of free volume nanoholes in ionic cross-linked CS are enriched by C and H atoms, which are associated mainly with the backbone (D-glucopyranose ring moieties) of CS molecule. This can be well explained that compact packing density of backbone of CS molecule chains are created in the vicinity of ionic cross-links sites, as the hanging groups ( $OH-C_3$ ,  $-NH_2$ ) are strongly bound to Pd. In addition, it is to be noted that a continuous decrease of  $I_3$  intensity is observed by PALS, this observation combined with the CDB result confirm the anion formed in the process of polymerization balanced the charge on the chitosan,<sup>45</sup> thus additional negatively charged chloride ions ligands existed in the surround of positively amino and metal cations are presumed to play a vital role in determining the annihilation of thermalized positrons. According to Wang C et al.,<sup>44</sup> chloride ions capture positrons to form the complex [CIPs], because the Ps affinities of Cl is positive so that its decomposition into Ps and Cl can be neglected, and this process can be described as follows:



that results in suppression of Ps formation, which can account for the decrease of  $I_3$  in the cross-linked CS

network.



**Fig. 9** Distribution of free volume nanoholes in CS and its complex. The solid lines are Gaussian fits to data.

From what has been discussed above, we may safely draw the conclusion that changes in chemical environment of palladium salt doped CS system were dramatically impacting positron annihilation and *o*-Ps formation, and further reflected in the analysis of the obtained positron annihilation parameters. These results show that it is not reasonable to evaluate the relevant change of free volume related microstructure using *o*-Ps intensity in palladium salt doped CS system, since it involves chemical effect on positron formation and annihilation. It is well known that polymer materials show a size distribution of local free volume that leads to distribution of *o*-Ps lifetimes around their mean. In this, in order to visually presents the effect of ionic crosslinking effect on the microstructure, the continuous analyses of the *o*-Ps lifetime have been performed using MELT, as shown in Fig. 9. For evaluating the distribution of free volume nanoholes, continuous lifetime distributions were calculated for CS and its complex, and the *o*-Ps annihilation rate distributions obtained from MELT analysis have been transformed to free volume size distribution based on the Tao-Eldrup equation [Eq.3]. The distributions were fitted to Gaussian distribution and full width at half maximum (FWHM) for CS, CSPD1, CSPD2, CSPD3 and CSPD4 were 12.2, 11.40, 16.30, 27.10 and 17.58 Å<sup>3</sup>, respectively. In the present case, only one peak has been obtained showing the overall distribution of nanoholes in all of the samples, and the peak position of the distribution shifts to lower value in CSPD1 and higher value in CSPD2, CSPD3 and CSPD4, which is consistent with discrete component analysis. In the former case (CSPD1), it is obvious that the nanoholes size distribution shows the overall shift of peaking at lower size compared to pure CS, which is attributed to the local enhanced ordered packing of chitosan chains. On increasing the loading of palladium salt, a more obvious broader distribution of free volume size centered at a higher value was observed, indicating the crosslinking effect can lead to evidently rearrangement of chitosan molecule chains, creating larger size free voids in the cross-linked CS network. The relative change in FWHM after incorporating palladium salt again indicates that the change of crystallinity of formed CS membrane can lead to variation in packing density of chitosan molecule chains. In addition, Fig. 9 shows a monotonously decrease in curve area of Gaussian distribution from CS to CSPD1 to CSPD4. This observation is well consistent with discrete positron lifetime data that a continuous decrease of *I*<sub>3</sub> intensity from 14.97% in pure CS to 6.927% in CSPD4, and hence further supports the chemical inhibition effect on *o*-Ps formation as mentioned above.

## 4. Conclusions

We report a transition metal salt doping study of positron annihilation in CS polymer. The strong interaction between Pd cations and CS molecules was observed to disrupt the original molecular packing, as seen from WAXD, FTIR and water-swelling analysis, resulting in rigidification and rearrangement of CS molecule chains in the process of film forming. Positron annihilation experiments have been performed in cross-linked CS as a function of the content of palladium salt. The *o*-Ps lifetime variations are interpreted in terms of free volume and

hole properties. PALS studies revealed ionic cross-linking induced alterations in the chain packing of CS at a microscopic scale, which is confirmed associated with the variational crystallinity of the ionic cross-linked CS by WAXD. The  $I_3$  intensity was observed to monotonic decrease with palladium salt loading primarily due to chemical inhibition effect. CDB measurements have been carried out to obtain more information about the chemical surrounding of nanoholes and positron annihilation characteristics in ionic cross-linked CS system. CDB data provided direct evidence of localization of positron wave function distributes away from the ionic crosslinking sites in cross-linked CS. CDB measurements along with PALS studies showed that positrons are not trapped at the polar groups and the chemical surrounding of free volume nanoholes in ionic cross-linked CS are enriched by C and H atoms, which are associated mainly with the D-glucopyranose ring moieties of CS backbone. In addition, negatively charged chloride ions ligands existed in the surround of positively amino and cations are supposed to result in suppression of *o*-Ps formation. Our results highlight the potential of PALS and complementary CDB technique in characterizing the microstructural and microenvironmental information in CS polymer. The present study should provide a backbone to probe local free volumes and related environmental element information in complex polymer such as Metal-Organic Frameworks (MOF) material in the future.

## Acknowledgements

The authors gratefully acknowledge the NSFC (No.11175191, 11475197, 11575205) of China for the support of this work.

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